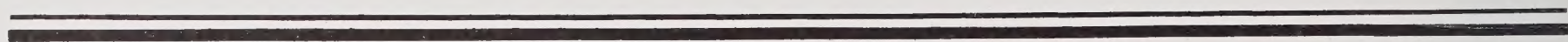

PROPERTIES AND USES OF TITANIUM, ZIRCONIUM, HAFNIUM,
NIOBIUM (COLUMBIUM), AND TANTALUM FOR THE
ARTIST METALSMITH

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Published and filed under the auspices of
Education and Research Department of
Society of North American Goldsmiths



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BIUM), AND TANTALUM FOR
THE ARTIST-METALSMITH

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ACKNOWLEDGMENTS—Special thanks to Vic Massey of Teledyne Wah Chang Albany for helping me locate a great deal of obscure information about the metals, and thanks to Ramona Solberg and John Marshall of the University of Washington for their encouragement.

ABSTRACT

Titanium and other refractory metals have recently been attracting the interest of artist-metalsmiths. While their primary use has been in terms of "coloring" via controlled thickness, oxide layer production; consideration of their physical properties, formability, and safety-health characteristics have largely been ignored. It is the purpose of this paper to deal with these considerations in the hope of presenting a framework on which further artistic experimentation and research can grow.

INTRODUCTION

The metals in consideration are pure metals * i.e., chemical elements. They are not allomorphs or alloys of other more familiar metals. One common property of these metals is their very high melting point; this has lead to the locution "refractory metals" for the group. While the American Society for Metals defines a refractory metal as any metal with a melting point higher than that of iron, cobalt, or nickel (c. 2800 deg. F) this would lead to a definition that would describe approximately sixteen pure metals. For practical purposes though, it is usually taken to refer to the nine metals of groups IVB, VB, and VIB of the periodic table: titanium (Ti)**, zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb)***, tantalum (Ta), chromium (Cr), molybdenum (Mo), and tungsten (W).

Unlike most metals used by artists these metals were not known to ancients. Their discovery as distinct metals/metallic elements dates from the late eighteenth to the early twentieth century. Most were first recognized only as oxides (or to use the archaism: "earths") because the technology to produce the pure me-

tal, or metal regulus, did not exist until approximately the turn of this century (Fig. 1).

Some of the physical properties of the metals are shown in Figure 2. Common properties are their high melting points, similar chemical properties, formation of a relatively inert oxide layer when heated (or simply by the action of air on freshly cut metal), they are also pyrophoric in air when strongly heated. While their mechanical properties differ considerably, they all become brittle and hard when heated in air due to oxygen absorption*. Their primary applications are in the aerospace, nuclear, chemical, and electronic industries.

*Other gases may be absorbed e.g., hydrogen and nitrogen forming hydrides or nitrides respectively, similar mechanical changes will occur.

FIGURE 1		
METAL	DISCOVERY AS AN ELEMENT	FIRST PRODUCTION AS PURE METAL
Titanium	1795	95% 1887, 99.9% 1910
Zirconium	1789	1914
Hafnium	1923	1923
Niobium	1801	small quantity c. 1900, large 1929
Tantalum	1802	c. 1903

The metals, with the exception of titanium, are scarce in the earth's crust**, but all are far more common than gold or silver (Fig. 3). Cost of the metals in the commercially pure

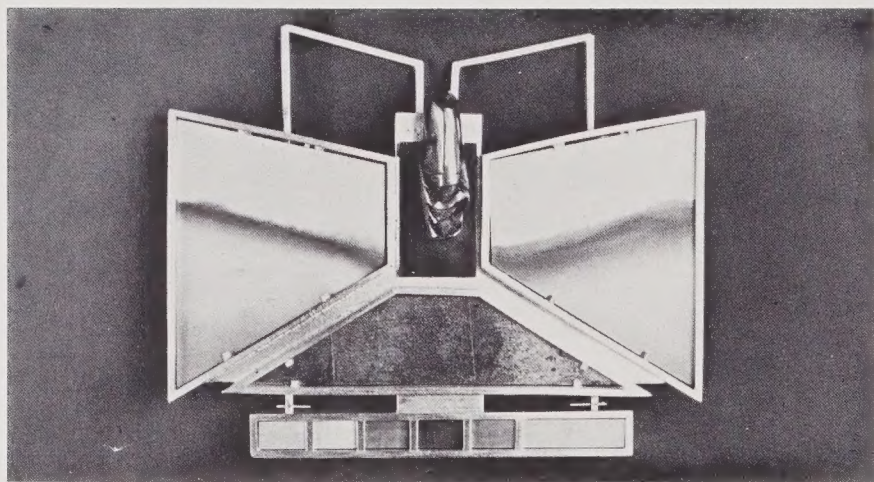
state, as sheet, is as follows:
Titanium, \$8-\$10/pound av.
Zirconium, \$15-\$25/pound av.
Hafnium, \$200-\$350/pound av.
Niobium, \$80-\$100/pound av.
Tantalum, \$80-\$100/pound av.
These prices will vary with supplier, quantity, thickness of sheet, form of mill product, and degree of purity.

**Titanium is the tenth most abundant element in the earth's crust being more common than carbon or sulfur.

FIGURE 2								
Metal	Melting Point	Density	Color	Percent Elongation	Tensile Strength	Yield Strength	Hardness	Annealing Temperature
Silver-fine	1761 F	10.49 a	silver	48-54%	18,200 b	7900 b	27c	572 F
Gold-fine	1945 F	19.32 a	gold	45%	18,500 b	Nil	25c	575 F
Titanium 99.2%	3035 F	4.51 a	lt. gray silver	28%	59,000 b	40,000 b	190 c	1100-1350 F
99.0%	"	"	"	25%	95,000 b	80,000 b	—	"
Zirconium 99.5%	3350 F	6.49 a	"	18%	41,500 b	25,000 b	110-180 c	1350-1450 F
99.0%	"	"	"	16%	53,500 b	31,000 b	—	"
Hafnium	4046 F	13.09 a	"	24%	55,000 b	20,000 b	190 c	1450 F
Niobium	4474 F	8.6 a	bright silver	30%	30,000 b	15,000 b	80 c	1450 F
Tantalum	5425 F	16.6 a	blue violet gray	40%	40,000 b	19,000 b	90 c	2000 F
Stainless steel—18-8	c.2500 F	c. 7.5 a	lt. gray silver	30%	75,000 b	45,000 b	c. 160	—
Aluminum 1100 series	1190 F	2.71 a	silver gray	40%	13,000 b	5,000 b	23 d	650 F
Copper DHP	1981 F	8.94 a	copper	45%	32,000 b	10,000 b	40 e	700-1200 F

All figures are approximate and represent an average if a range was given; anisotropic properties have been neglected.
a—grams/cc c—Vicker's or Diamond Point hardness e—Rockwell "F" hardness
b—pounds/in² d—Brinell hardness 500kg

*Pure should be taken to mean commercially pure which is usually 99.0-99.5%. Scientific/chemical purity is usually considered to be 99.9% or higher.
**These are the internationally accepted chemical symbols/abbreviations for the metal/element.
***Also known as columbium (Cb), however niobium is preferred.



Joseph Hall, sterling, titanium and steel 3"x2"

PRODUCTION OF THE METALS

The production of these metals on a significant commercial scale did not begin, in most cases, until the last thirty years. This was not so much a limitation caused by technology but rather by lack of demand. Only with the advent of the aerospace and nuclear industries, and the recognition of their cost effectiveness by the chemical industry for handling corrosive substances did their production substantially increase.

Production of the metals from ores is quite complicated; with special problems arising in separating zirconium from hafnium, and niobium from tantalum. This is exacerbated by the fact that even though the metals are not exceptionally rare in nature their ore deposits are very widely distributed in low concentrations throughout the world. In brief, the production of the metals from ore is a three part process: the first step is the formation of a pure metal compound, the second step is the chemical reduction of this compound to the pure metal, and the third step is the consolidation of the metal by melting. This may be illustrated by a simplified account for the production of titanium:

Step 1: $\text{TiO}_2 \xrightarrow{\text{C}} \text{TiC}_{14}$; Formation of a reducible titanium compound from titanium dioxide ore.

Step 2: $\text{TiC}_{14} \xrightarrow{\text{Mg}} \text{Ti} + \text{MgCl}_2$; Formation of titanium metal by chemical reduction of titanium tetrachloride by magnesium.

Step 3: Conversion of the titanium metal sponge to a titanium ingot by melting.

The process is more complex with the separation of hafnium from zirconium, or niobium from tantalum; in both cases more subtle chemical differences are used e.g., differences in solubility of analogous compounds, to achieve the separations.

An interesting aside here is the process used to melt the metals. Because of the extremely high melting points and reactivity with oxygen of the metals conventional melting techniques cannot be used. This problem is avoided by the two most commonly used melting processes: consumable electrode vacuum arc melting

and electron-beam melting. In the first process an electrode composed of welded refractory metal sections is produced. The electrode along with a water cooled mold is then placed in a melting chamber. The chamber is then evacuated to a pressure of 10^{-2} mm of mercury. An arc is struck between the refractory metal electrode

FIGURE 3

METAL	PERCENT IN EARTH'S CRUST
Silver	10-8%
Gold	10-9%
Titanium	$6 \times 10^{-1}\%$
Zirconium	$4.5 \times 10^{-4}\%$
Hafnium	$9 \times 10^{-6}\%$
Niobium	$2 \times 10^{-3}\%$
Tantalum	$2.1 \times 10^{-4}\%$
Aluminum	8%

and the mold melting the tip of the electrode and maintaining a shallow pool of the molten metal in the mold. The metal electrode is lowered towards the pool in the mold as it is consumed and the mold filled. The arc is then stopped and the ingot allowed to cool before removal and milling. Ingot size may be one foot in diameter and six to eight feet long (Fig. 4). In electron-beam melting a welded or sintered bar of the metal is forced into the path of a high velocity electron beam (produced by an electron gun) which both melts the metal and maintains a shallow pool of the molten metal in a water cooled mold directly below the melting bar. The ingot is continuously lowered through the vacuum chamber as it is formed by the melting of the bar. The ingots may be one foot in diameter and up to ten feet long (Fig. 5).

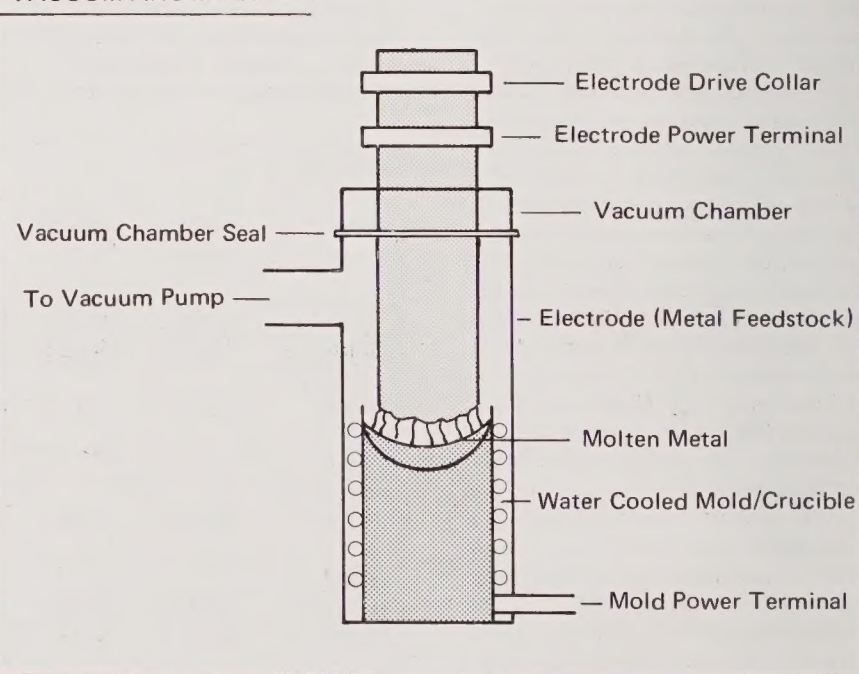
COLORING OF THE METALS—NATURE OF THE COLORS

The surface of these metals may be oxidized to produce brilliant colors which are permanent and reasonably durable. This has been, with justification, the major use of the metals by artists. It should be understood though that the colors

do not derive from any inherent color of the oxide, but rather from an interaction of the colorless oxide film with light through a phenomenon known as interference (this is the same phenomenon that gives colors to soap and oil films). To understand these interference colors, some background in the physics of light is required. The contemporary paradigm of the nature of light states that it is composed of particles (photons) that exhibit wave-like characteristics (termed the "wave particle duality" of light), but for our purposes it is sufficient to simply consider it a wave. Being a wave it will

if they combine "out of phase" little or no light will be seen. Assuming that two waves of the same wavelength arrive at the surface of the oxide film, say one immediately after the other, one could be reflected from the top surface of the film and the other undergo defraction and be reflected up from the bottom surface of the film (the metal-metal oxide film interface). If uniting of the two waves then occurred to form a single ray** the two waves could be either in phase or out of phase — if they were 180 degrees out of phase they would nullify each other (because of destructive interference) and the eye

FIGURE 4
VACUUM ARC MELTER



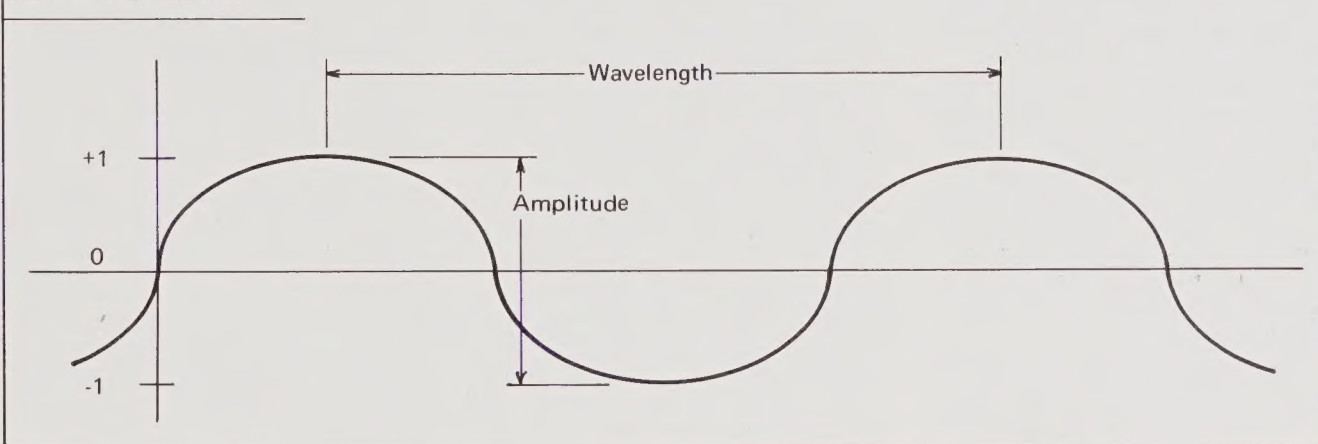
have the characteristics of waves and undergo physical phenomena associated with waves e.g., it will have wave length and amplitude, undergo reflection, refraction, and interference (and other effects). Taking any one wave an oscillation is characteristic of its pictorial representation: one complete "S" shaped oscillation defines the wavelength (Fig. 6). Interference occurs when two light waves combine. If they combine when the waves are "in phase" light is seen;

*If the crests and troughs of the waves coincide they would be termed in phase; if they did not they would be out of phase up to a maximum where one's crest is at the other's trough, they are termed 180 degrees out of phase.

**A ray is composed of many individual waves traveling in exactly the same direction on an imaginary line through space.

would not perceive any light reflecting from the surface and it would appear black (assuming that it was the only light incident to the metal surface). White light is obviously not monochromatic i.e., composed of only one wavelength, instead it is composed of the red, green, and blue wavelengths/band-widths. If only one of these colors is destructively interfered with, the reflected color would be the combined result of the other two according to additive color theory e.g., if only green underwent destructive interference the resultant color would be blue+red forming magenta/purple. The thickness of the oxide film determines what colors undergo destructive interference (other factors also play a role: angle of incidence of the light; index of refraction of the oxide film, color of the parent metal, and others; however, these are usually out of the artist's control after selecting the metal). *Thus control of the oxide layer thickness will dictate its color.*

FIGURE 6
WAVE PROPERTIES



COLORING OF THE METALS— PRODUCTION OF THE OXIDE FILMS

All of the metals react with oxygen to produce oxide films/layers (Fig. 7). The two principle ways of producing the films are by direct heating of the metal, and by anodizing. In the heating method the oxide layer is produced by simply playing a torch over the surface of the metal. Anodizing is the process of oxidizing the metal electrolytically, a process simi-

lar to plating*. Both methods aim at producing a film of controlled thickness. It should be understood that the colors cannot be mixed like paints; the colors are limited to a standard color series (Fig. 8), by the laws of physics. Variations in intensity of the color can be achieved by varying the finish of the metal surface before oxidizing (see finishing). **HEATING METHOD**

Heating is the easier and the more limiting of the two techniques. The first limitation is that niobium and tantalum do not form oxide films capable of producing colors by this method, instead they form a gray or black oxide layer. The second limitation is that of control of the color and its precise placement on the metal. These problems arise because of the difficulty of stopping the heating when the desired color is achieved, and of conduction of heat to undesired areas on the piece.

Procedure for heat coloring: (1) select the surface finish for the parent metal (see finishing); (2) thoroughly clean the metal surface. Wash in a hot ammonia-detergent-water solution. Rinse in water. Degrease with methylethyl keton, denatured alcohol, acetone, etc. (denatured alco-

hol is probably the safest); (3) place the metal on a clean non-heat-conducting material e.g., fire bricks or charcoal, and heat. Colors will follow the standard color series as the heating proceeds varying with oxide layer thickness: a thicker oxide film being produced where the heating was strongest.

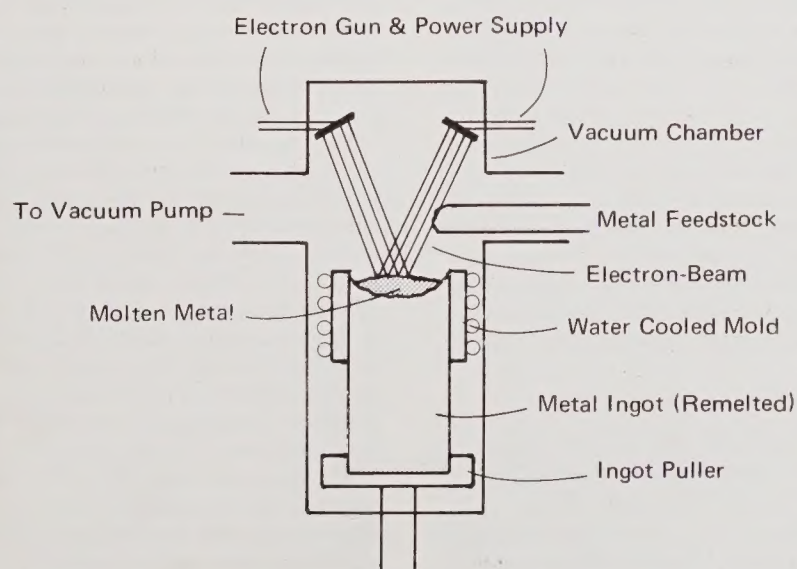
The type of air-gas or oxygen-gas torch used seems to make little difference. An oxygen-gas system with a very small hot flame can more easily produce localized colors; on the other hand, it is more difficult to get broad areas of even colors with this kind of torch than a cooler more broad flamed gas-air system. A kiln, with a strongly oxidizing environment, can be used, but observing the color changes on the metal is more difficult.

Of the metals amenable to flame coloring, titanium seems to produce the most pleasing range of colors for all surface finishes. Zirconium and hafnium produce brilliant colors when polished, especially chemically polished, but appear rather desaturated and dull with most other finishes.

ANODIZING METHOD

As mentioned earlier, anodization is electrolytic oxidation. It is a process similar to electroplating except nothing is plated; instead water is disassociated into hydrogen (at the cathode) and oxygen (at the anode). The oxygen oxidizes the material at the anode. Briefly, the work-piece is the anode surrounded or immersed in

FIGURE 5
ELECTRON BEAM MELTER



*A common example is the anodizing of aluminum. However, in aluminum the colors arise from dyes embedded in the oxide layer during the process, not from interference effects.

an electrolyte with an inert metal used as the cathode. Current is supplied from a power source that can produce a wide range of variable voltage. At any voltage there is a specific color that will form because voltage is proportional to oxide layer thickness (Fig. 9). All of the metals can be anodized with varying results. The anodizing process gives the artist far greater control in selection and placement of the desired colors on the metals (the use of selective masking further enhances control [see masking/resists]).

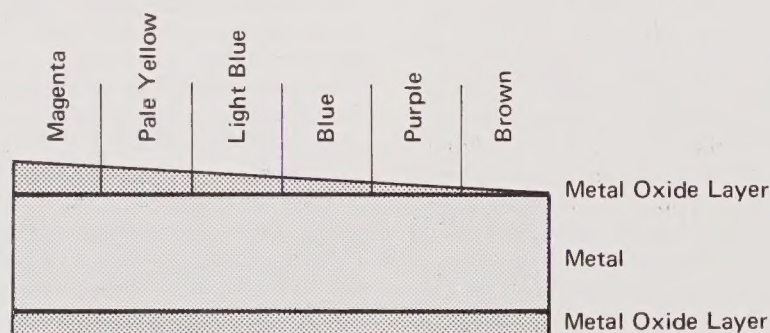
The equipment needed for anodizing consists of an AC* or DC power source capable of producing variable voltages from 0-120 or 0-140 volts, an electrolyte, and depending on the technique, either a container for the bath or an applicator for the electrolyte. AC power sources are recommended because they are both easy to build and fairly inexpensive. From my limited experience with

DC sources, I can see no difference in the quality of the colors. Conventional electroplaters are generally not suitable because their maximum voltage output is usually only 15 volts.

My AC anodizer is shown in Fig. 10a; it is 9"x5"x6", weighs 7 pounds, and cost approximately \$45.00 to build. Fig. 10b shows the inside of the unit with major components labeled. Fig. 11a is a schematic wiring of the circuitry. Fig. 11b is a component wiring diagram describing the unit more qualitatively. The heart of the unit is a variable auto-transformer with 120 or 140 volts output at 5 amps (the maximum output is dependent on one's choice in connecting the transformer). A "plug-in" voltmeter was added for convenience, but one was really not needed, because the transformer comes with a dial indicating percent output (this could be calibrated for specific colors rather than relying on a voltmeter e.g., 15% output could be a deep blue).

FIGURE 7
OXIDE LAYER ON METAL

(colors vary with thickness)



Not To Scale

*There is no true anode or cathode in an AC system; the terminals alternate between being positive and negative. Oxidation will still occur providing it is not reduced when it becomes the cathode. This is a simplified explanation. The terms anode and cathode will be used for both AC and DC systems, but they strictly apply only to the DC system.

FIGURE 8		STANDARD COLOR SERIES	FIGURE 9
		COLOR OF OXIDE FILMS	
HEATING METHOD FIRST-THINNEST		ANODIZING METHOD FIRST- THINNEST	
AMT. OF HEAT		VOLTAGE (AC)	
Least Heat	Very Light Yellow	5	
	Yellow Brown	10	
	Purple	15	
	Blue (Dark)	20	
	Blue (Light)	25-30	
	Pale Green-Gray Blue	35-40	
	Pale Yellow and Pale Green Blue	40-45	
	Yellow	45	
	Yellow and Pale Rose	50	
	Magenta	55	
	Deep Green Blue with Magenta	60	
	Deep Blue Green with Magenta	65	
	Magenta and Gold	70	
	Magenta and Green	75	
	Blue Greens with Magenta	80-90	
Blue Greens	90-100		
Spotty Green Gray	105		
Most Heat	Grays	115+	

These colors are for titanium with an ammonium sulfate electrolyte; colors on other metals will be similar with certain ranges more brilliant on some metals. Colors are subjective and not from analytical tests of reflectance.

ELECTROLYTES-CATHODES

The electrolyte I now use is the one suggested by James Brent Ward*, it is a 10%, by weight, ammonium sulfate and water solution. A complex electrolyte used by Teledyne Wah Chang Corporation works very well on zirconium and hafnium**. Other electrolytes are also acceptable e.g., copper sulfate-water and sodium carbonate-water, but the ammonium sulfate-water electrolyte is recommended. My cathode is usually a piece of scrap titanium, but certain stainless steels are also satisfactory. The electrolyte keeps well in a stoppered glass or plastic bottle.

*James Brent Ward, *Craft Horizons*, "Titanium: Metal of Many Colors", pp 20 and 21, August 1977.

**Percent by volume: granular citric acid 1.0%, Conc. Phosphoric acid 4.0% Lactic acid 8.0%, Glycerol 15%, Water 26.5%, Methanol 45.5%.

It does not require maintenance as plating solutions do, and can simply be discarded when it becomes contaminated or exhausted (a solution is exhausted when the colors are no longer vivid or they require higher voltages to achieve the same color). The greatest cause of contamination comes from the cathode dissolving (titanium cathodes do not dissolve).

Procedure for anodizing: (1) select surface finish for the parent metal (see finishing); (2) clean as in step 2 of heat coloring; (3) make sure that the power is off on the anodizer. Connect a scrap piece of titanium, as the cathode, to one of the leads of the AC anodizer — if DC is used it must be connected to the cathode lead. Connect the piece to be anodized to the other lead; (4) suspend both pieces in the electrolyte making sure they do not touch each other (shorting would occur if they did touch); (5) the anodizer is turned on and the voltage increased until the desired color is obtained (Fig. 9). If parts of

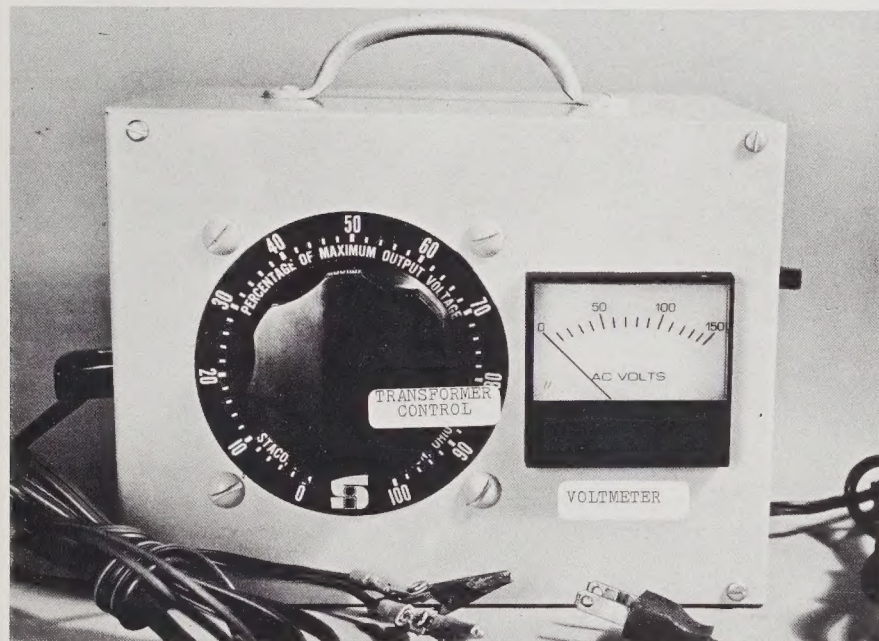


FIGURE 10a

the piece are not stopped-out with a resist (see resists) the entire piece will be uniformly colored. *The transformer is set back to zero volts and the anodizer is turned off before removing the piece from the electrolyte.* (6) the piece is rinsed in water and dried.

There are several variations on step 5 that produce other attitudes: (1) a uniform color oxide film can be produced as described above; (2) areas can be stopped-out with resist allowing only the areas exposed to the electrolyte to be oxidized; the resist can then be removed and a new area stopped-out allowing it to be oxidized.

NOTE: On re-exposure to the electrolyte at a higher voltage, a color formed at a lower voltage will become the higher voltage color. A higher voltage color will not become a lower voltage color on the same re-exposure e.g., a blue formed at 25 volts would become green if re-exposed at 85 volts; conversely, a green formed at 85 volts would stay green if re-exposed at 25 volts. Also, length of the exposure does not seem to influence the color. Starting with the highest voltage color required for the piece is recommended, this will largely eliminate the risk of one color transforming into another on re-exposure to the electrolyte.

(3) An artist's paint brush with a metal ferrule and wooden handle (or other electrical non-conductor) can be connected to the anodizer at the metal ferrule and used as the cathode. The work-piece is the anode. The voltage for the desired color is selected, the brush is dipped in the electrolyte, and the color is painted on the work-piece — anodization takes place between the brush, via the electrolyte, and the piece. The brush will need frequent re-dipping in the electrolyte, especially at the higher voltages where the heat generated by the electricity will cause the electrolyte to boil and rapidly evaporate. Occasional dipping of the brush in pure water will dissolve salts that build up during the anodizing. The brushes will also burn up, and the glue holding the bristles in place melt or dissolve because of the high temperatures generated. Nylon brushes seem to be more resistant than natural bristle brushes. (4) All of the above techniques lead to an oxide layer of uniform thickness forming one color. A wedged shaped oxide film can be formed by immersing the work-piece in a container of electrolyte and pulling the piece out as the voltage is varied (a titanium cathode is also immersed in the container). The results look somewhat like an oil slick on water but

the range and placement of colors can be controlled quite well with practice. **WARNING**

When working with any of the techniques the artist is handling electrically charged equipment in a wet environment: all work should be done on a wooden or other non-electrically conducting surface, rubber gloves should also be worn.

RESISTS

Almost any of the resists used in etching or plating can be used in the anodizing process. Consideration of the resist's ability to stand up to hot solutions should be noted. Hardground, asphaltum varnish. Microstop $\text{\textcircled{M}}$, Microflex $\text{\textcircled{M}}$, Micropeel $\text{\textcircled{M}}$, wax, and various tapes are all acceptable. Etched metal, having a lightly toothed

protection from touching the piece needs: body oils are absorbed on the sandblasted or etched surfaces and mute the colors, highly polished surfaces seem to scratch more easily.

SANDING AND BUFFING: The titanium metals are quite hard and are best treated like stainless steels. Sanding with silicon carbide papers and buffing with tripoli and stainless steel rouges works well. Niobium and tantalum are "gummy" metals. Sanding with emery and buffing with tripoli and red or white rouge is usually satisfactory. With all of the metals though, scratches are very difficult to remove and care should be paid to avoid unnecessary scratching.

ETCHING: Etching is usually done with a dilute hydrofluoric acid

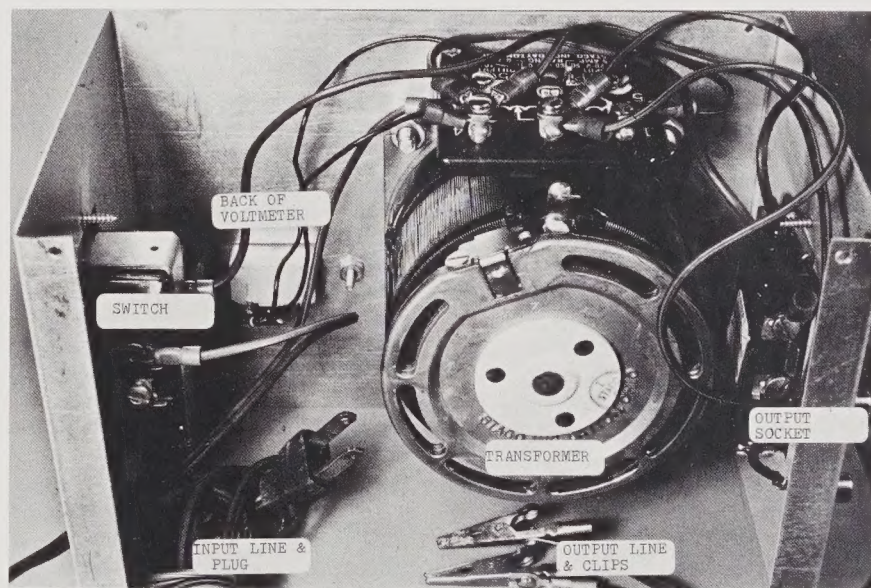


FIGURE 10b

surface, makes it difficult to get an extremely sharp line with any lacquer-like resists, hard ground and asphaltum work best with this type of surface.

FINISHING

The finish on the parent metal will greatly affect the intensity of the reflected color. Sandblasting gives a subdued, almost flat, color with far less chromatic intensity than a highly polished surface; a lightly etched surface lies somewhere between these two extremes. The selection of the finish places some restraints on the

solution or a hydrofluoric acid-nitric acid bath. The metal's oxide film must be dissolved for the acid to attack the metal. All solutions are used at room temperature. Great care should be taken in mixing and storing the solutions because of their highly corrosive nature: wear rubber gloves and a face shield when mixing or using; strong positive ventilation is almost essential (a chemical lab type fume hood is recommended). Do not smoke because flammable hydrogen gas is produced during the etching process.

Etchant No. 1 for titanium, zirconium*, and hafnium*: 10 ml Hydrofluoric acid** + 100-200ml Water.

Etchant No. 2 for titanium, zirconium*, and hafnium*: 90ml Nitric acid + 10ml Hydrofluoric acid + 1000 ml Water. This is the best etchant I have used for titanium.

Etchant No. 3 for niobium and tantalum: 50ml Hydrofluoric acid + 25ml Nitric acid + 500ml Water. If the reaction is too vigorous dilute with water.

Chemical bright-dip for zirconium, hafnium, and tantalum (courtesy of Teledyne Wah Chang Corp.): 1st dip in the following solution: 125ml hydrofluoric acid + 500ml Nitric acid + 500ml water. 2nd rinse the piece in running cold water. 3rd dip in the following solution: 500ml Nitric acid + 500ml Water (if the piece does not have dark stains this step may be omitted). 4th rinse in water and dry.

Chemical bright-dip for niobium (courtesy Teledyne Wah Chang Corp.): 1st dip in the following solution: 300 ml Nitric acid + 300ml Sulfuric acid + 100ml Hydrofluoric acid + 300ml water. 2nd rinse in running cold water. 3rd dip in the following solution: 350 ml Nitric acid + 200ml Sulfuric acid + 350ml Water. 4th rinse in water and dry. This dip has been recommended, I have no personal experience with it.

Titanium can also be photo-etched using a hydrofluoric acid etch or a hydrofluoric acid-nitric acid etchant and an appropriate photosensitive resist e.g., Kodak Metal Etch Resist or Kodak Thin Film Resist. It could be assumed that the other titanium metals, and probably niobium and tantalum, could be similarly etched.

*Zirconium, and to a lesser extent hafnium, often form black stains in this etchant. A water rinse followed by a dip in 50% Nitric acid-Water will usually remove the stains.

**All concentrations are for standard concentrated acids. Dipping the titanium metals in concentrated hydrofluoric acid without dilution may cause an explosion (see health/safety section).

PLATING

The metals cannot be plated on other metals except in a molten salt electrolyte, and then only with difficulty. If a thin plating is required explosively clad materials are available from some suppliers. The metals can be plated with other metals if an immersion coat of copper or zinc is first applied. The following solutions are from the Metal Finishing Guidebook and Directory*:

SOLUTION NO. 1: 200g/liter Copper Sulfate + 480g/liter Sulfuric acid + 24g/liter Aluminum Sulfate + 0.1% Wetting agent. The solution is used at room temperature. The metal should be thoroughly cleaned before immersion.

SOLUTION NO. 2: 100g/liter Sodium Dichromate + 5g/liter Copper Sulfate + 50ml/liter Hydrofluoric acid. The solution is used at 210 degrees F. Thoroughly cleaning is required before immersion. A note is made concerning this solution that zinc sulfate may be substituted for the copper-sulfate resulting in better adhesion.

ENAMELLING

Enamel does not adhere to titanium, it will flake off in large pieces on cooling. A possibly explosive combination may result if an enamel containing borax is applied to zirconium (hot zirconium and borax have been known to explode). *Caution should be exercised in any experiments with hot metals and enamels (or any chemical).*

FORMABILITY

A set of numerical parameters, often referred to as "mechanical properties" in metals data books, can be used to give a more objective feel to an unfamiliar metal than statements like, "it's similar to copper", similar is a vague word. A reference to the parameters of familiar metals would enable the metalsmith to understand the working properties of unfamiliar metals. The parameters aid in accurate communication about the physical character of metals. Fig. 2 lists the properties of the metals in

*The Metal Finishing Guidebook and Directory, p. 161, 1977, Metal and Plastics Publications, Inc.; Hackensack, NJ.

FIGURE 11a
SCHEMATIC DIAGRAM OF ANODIZER

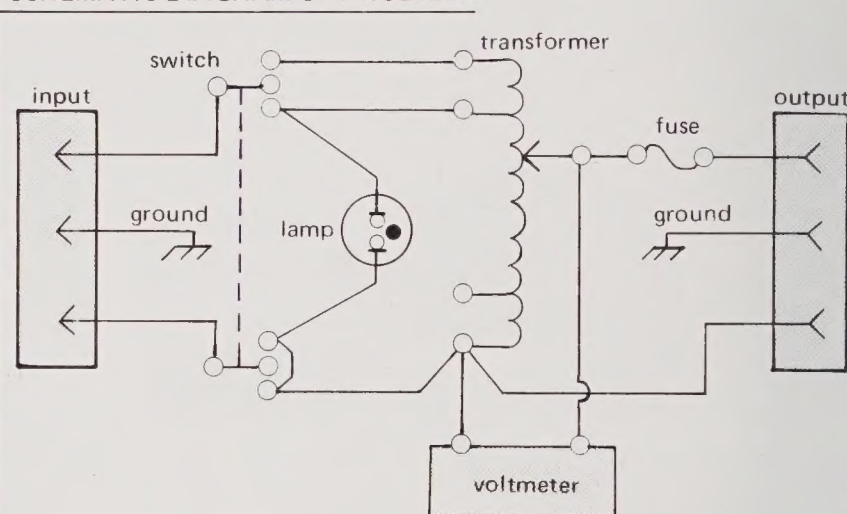
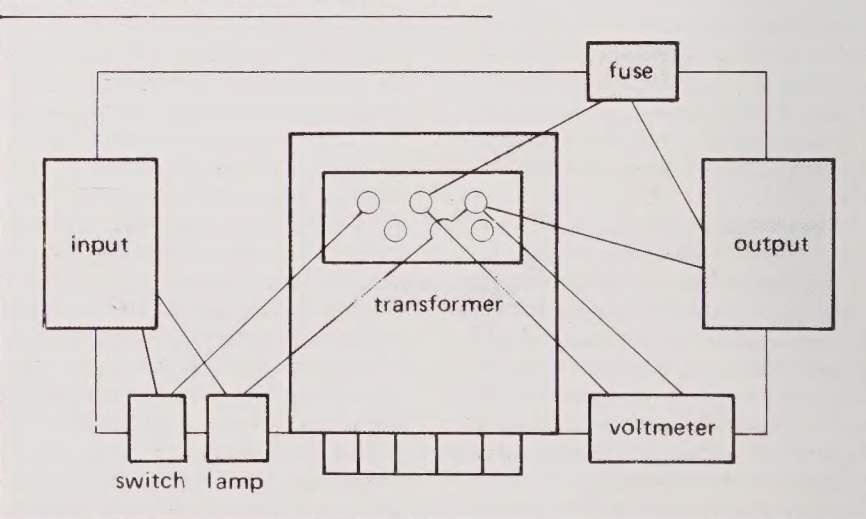


Figure 11a courtesy of Theodore Swift and Staco, Inc. Fuse should match maximum output of the transformer.

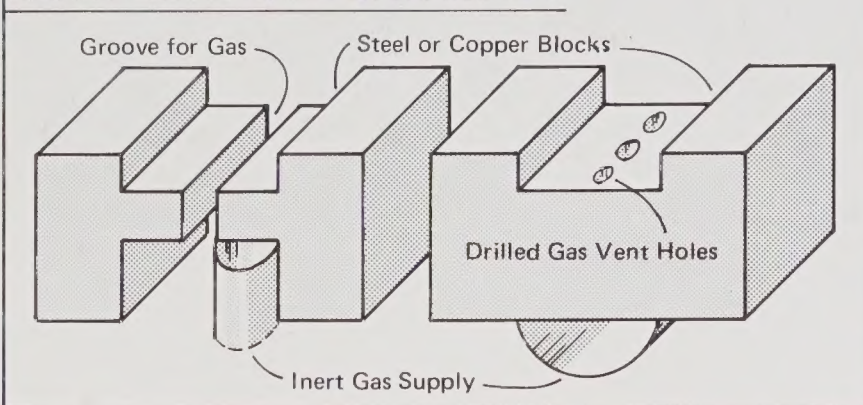
FIGURE 11b
COMPONENT DIAGRAM OF ANODIZER



this paper along with the same properties/parameters for more familiar metals (notice should be paid in comparing scientifically pure metals with commercially pure metals: the very pure scientific grade may be much more ductile than the commercial grade). Unfortunately, qualities like ductility and malleability are not measured by a single parameter, there is also some arbitrariness (subtleties) as to what parameters define these characteristics. However, two useful indices are per-

cent elongation for ductility, and yield strength for malleability. The greater the percent elongation the greater the ductility. Yield strength is a measure of the minimum force needed to permanently deform (shape) a piece of metal i.e., to produce "plastic deformation" (forces less than this will produce no permanent deformation and the piece will simply spring back to its original form when the force is relieved, this temporary deformation is termed "elastic deformation").

FIGURE 13
BACK-UP GAS FIXTURES FOR TIG WELDING



FORMING—When forming the metals two problems are immediately encountered: (1) High purity metals are essential. If as little as 0.2%-0.3% oxygen, nitrogen, or hydrogen is present the formability may be halved (compare the differences in yield strength for the two purities of titanium and zirconium in Figure 2). (2) There is no way for a conventional metalsmith's shop to anneal the metals. The metals must be annealed for a period of several hours in a very high vacuum. There appears to be no easy way around this problem (a suggestion of annealing in a kiln [electric] filled with inert gas e.g., argon, is unsatisfactory because of trace amounts of oxygen, etc. in the gas would cause severe embrittlement). Some distributors may be willing to anneal work for you if you send the piece in to them — check with them first before you try this approach.

The titanium metals are much more difficult to work than the metals most metalsmiths work with. Work hardening also seems to occur more rapidly than with conventional metals. The metals are usually harder than most forming tools e.g., mandrels, hammers, stakes, unhardened dies, etc., and thus will damage these tools: hardened tools should be used. If forming is required, specify the highest purity metal obtainable, fully annealed, and in the thinnest gauge aesthetically possible. Hot working is possible, but one should be fully aware of the pyrophoric nature of the metals; the thick oxide coat formed with hot working will have to be mechanically removed or etched away. Spinning is possible if there are no sharp radii curves or angles, but again the problem of annealing will arise.

Niobium and tantalum are more amenable to forming than the titanium metals (note the increase in percent elongation and decrease in yield strength vis-a-vis the titanium metals). Annealing is still a problem but the initial malleability will allow for greater forming. Again, the metals must be of highest purity and fully annealed. Chasing and repousse are possible with thin metal (26-28 gauge); pitch should be removed with solvents rather than flame to avoid hardening. Spinning is possible, but the metals thin easily.

FIGURE 12

Metal	Turning Feed ipr	Speed sfm	Depth in	Tool Geo- metry	Drilling Feed ipr	Speed sfm	Tool Geo- metry	Both Coolant
Titanium	0.015 r 0.007 f	100 r 110 f	0.150 r 0.025 f	1) 5 2) 0 3) 8 4) 0.125" 5) none	0.002 1/8" hole 0.006 1/2" hole	50	135 1/4" 118 1/4"	Soluble type heavy flood CIMCOOL or SOLVAC
Zirconium	0.020 r 0.005 f	80-100r 150 f	0.125- 0.025r 0.010- 0.040 f	1) 10 2) 15 3) 10 4) 0.030" 5) yes 3/16"	0.005- 0.010	40-60	118	As titanium
Hafnium	AS ZIRCONIUM							
Niobium	0.008- 0.012 r 0.005 f	60-80 r&f	0.125 r 0.030 f	1) 30-35 2) 15-20 3) 5 4) 0.025" 5) no data	AS COPPER			Air, Rapid Tap, etc.
Tantalum	0.008 r 0.005 f	50-60 r&f	0.060 r 0.015 f	1) 5 2) 10 3) 5 4) 0.020" 5) no data	AS MILD STEEL	30-40	118	as niobium
r—roughing cut f—finishing cut		Tool Geometry:		1) Side rake 4) nose radius	2) Back rake 5) chip breaker	3) Side and end clearance		
Carbide tools are preferred for the titanium metals: high speed steel tools for niobium and tantalum.								
CAUTION—ALL OF THE METALS ARE PYROPHORIC IN AIR!								

CUTTING ACTIONS—Cutting actions like sawing, filing, drilling, and tapping are considerably more tedious and damaging to tools with the titanium metals than with the precious metals. A good supply of replacement tools, especially drills and saw blades, should be kept on hand — if the tools do not break they will dull out. Frequent use of light oils, e.g., sewing machine oil, is recommended for hand tool processes and essential in machine tool use. Coarse files and saw blades are recommended. Niobium and tantalum resemble hardened copper with regard to cutting actions, and except for galling, present no special problems.

MACHINING—The data given in Fig. 12 lists recommended tool geometry, and cutting feeds and speeds for the metals. All of the metals, but especially tantalum, have a tendency to gall or seize and subsequently work

harden. If galling does occur the tool clearance angles should be increased. Carbide tools are recommended for the titanium metals; high speed tools for niobium and tantalum. Heavy use of coolant is required with the titanium metals and desirable with niobium and tantalum because of the poor heat conductivity of the metals. *Caution:* all of the metals are pyrophoric, when in a finely divided state such as lathe turnings — **AVOID ACCUMULATION OF DUST, CHIPS, AND TURNINGS.** Teledyne Wah Chang Corp. suggests storing chips etc. away from the working area in a nonflammable container filled with water with a thin layer of oil floating on it to reduce the water's evaporation. If a fire does occur do not use water; use dry sand (see health and safety).

SOLDERING AND WELDING—None of the metals can be soldered

or brazed*. All must be welded in an inert gas atmosphere. Tungsten Inert Gas (TIG) welding is the most commonly used process (plasma arc, and electron beam welding may also be used). A complication arises though in that the back of the weld must also be shielded (Fig. 13) shows a couple of possibilities for running inert gas to the backside of a piece. Preferable to back shielding is welding in an inert gas filled chamber (the chamber is first evacuated and then filled with inert gas). The units are usually built to the specifications of the user at a cost of \$1000 and up. The work and torch are sealed in the chamber and the operator handles the torch via rubber gloves sealed to the frame. Extra high purity inert gas should be

*Some experimentation using copper plated metal with exotic filler rods/solder has been done, success has been limited.

used or embrittlement might occur through absorption of trace reactive gases. A good weld will not show any oxide coloring.

Typical TIG set-up:

Shielding gas — Argon plus back shielding

Electrode—2% Thoriated tungsten

Welding current—DC straight polarity

Chill bars recommended

Gas flow rate—approximately twice stainless steel

Amperage—approximately twice stainless steel

Metal must be clean and degreased. The metals do not weld well to other metals because of the formation of intermetallic compounds and subsequent joint embrittlement. Consultation with a welding engineering is strongly recommended before attempting any welds.

CASTING—Casting is out of the question in a metalsmith's shop. The metals will burn violently in air long before the melting temperature is approached; secondly, the temperatures required for melting cannot be achieved except by special processes (see production of the metals). Suppliers can give the artist names of commercial casters, however, the cost and design limitations will probably be prohibitive.

HEALTH AND SAFETY—As of January 1979, the toxicity of these metals in their pure or oxidized state is thought to be minimal: this may not be true for their compounds, some of which are known to be toxic. Toxicity may be lower than that of many metals commonly used by metalsmiths; however, this is not an endorsement or certification of their safety. In some cases, as with niobium and hafnium, there is very little data on prolonged contact with the metals or compounds. When working with any new or exotic material the artist must make it his or her duty to thoroughly research the health hazards of the materials AND up-date this information frequently. The dusts of the metals should be avoided (with the same degree of caution used with other conventional metals.) Titanium and tantalum are both used in implants for human surgery, this would seem to indicate some degree of safety. All metalsmiths should be familiar with the following book which lists known health hazards of materials:

Dangerous Properties of Industrial Materials, 4th edition 1975, N. Irving Sax, Van Nostrand Reinhold Co.; New York, New York.

The major safety problem stems from the pyrophoric nature of the metals. This is not of any real significance when dealing with sheet (except foil) or wire, but should be considered a definite problem with the dusts and metal turnings — avoid accumulations of either. The titanium metals, especially zirconium, react quite violently with concentrated hydrofluoric acid, the hydrogen formed during the reaction may ignite by the heat of the reaction. None of the metals should be allowed to contact fluorine or chlorine gas. Zirconium has been known to explode when heated with borax (the component of some enamels and most hard solder fluxes) and some alkali hydroxides. Titanium may form an explosive compound when mixed with red-fuming nitric acid; also avoid any contact of titanium with liquid oxygen due to a very high explosion danger. This last caveat may seem silly, but metalsmiths tend to be extremely curious in searching for new materials, or combinations of materials, with which to better express themselves — liquid oxygen may be a tame curiosity in the end. When dealing with new combinations of materials in a chemistry-like situation, or under any extreme condition of heat, or pressure, etc., caution is required. The National Fire Protection Association (NFPA) publishes an excellent guide book on how to safely deal with new (and familiar) materials, it also includes an especially good section on hazardous reactions between materials: *Hazardous Materials*, National Fire Protection Association, 470 Atlantic Ave., Boston, MA, 02210.

SOURCES FOR THE METALS—Fig. 14 is a list of known or recommended suppliers. There are many other suppliers throughout the country. Check the "Yellow Pages" of any major city's phone book, or look in the *Thomas Register* under the name of the metal desired. Most suppliers will give the names of local fabricators who buy from them; these fabricators are a good source of information and scrap (scrap is often available at 1/2 to 1/4 the cost of new

FIGURE 14

COMPANY-ADDRESS	METALS SOLD					COMMENTS
	Ti	Zr	Hf	Nb	Ta	
Astro Metallurgical 3225 Lincoln Way W. Wooster, OH 44691 (also, Los Angeles)	x	x			x	Friendly, accept small orders \$35-\$50 min., supplier
Fansteel Metals 1 Tantalum Place North Chicago, IL 60064				x	x	Usually \$100 min. Primarily sell tantalum, manufacture/supplier
Gehning, Inc. P.O. Box 0, Dept. T Syosset, NY			x			
Leico Industries 250 W. 57th Street New York, NY	x	x	x	x	x	
Teledyne Wah Chang P.O. Box 460 Albany, OR		x	x	x	x	Usually \$100 min., very friendly, large manufacture/supplier
Futura Titanium P.O. Box 5004 West Lake Village, CA 91359	x					no direct information, but recommended by others
Timet 400 Rouser Rd. Pittsburgh, PA	x					not especially friendly on small orders, \$100 min., large manf.
Titanium Sales Corp. 17T Industrial Rd. Fairfield, NJ 07006 Also offices in: Montreal, Canada; Sao Paulo, Brazil	x					
Each company's minimums may change at any time; different types of mill products are usually not combinable to reach minimum order. My best experience has been with Astro Metallurgical (Los Angeles office) and Teledyne Wah Chang.						

material), but DO NOT expect them to be familiar with metalsmithing terminology or always pleased to give free advice. When buying new material two problems will be encountered: (1) Most firms have a minimum order which is usually between \$50 and \$200, a \$100 minimum is normal. There are generally no price-lists; call for quotes. (2) The availability of mill products varies considerably. Most suppliers cannot change the shape or thickness of sheet or wire, and will not, if they could, on any order approaching a minimum order. Sheet, plate, round wire, and extruded tubing/pipe are standard mill products. Special shapes are generally made to order, but only on industrial size orders. I recommend purchasing scrap from fabricators for any initial experiments.

CONCLUSION—A caveat. The refractory metals are immediately seductive because of their "easy" colorability, but beyond the color lies form, and hopefully within the form is content. They have a tremendous potential for producing pieces that are superficially extraordinary. The question often arises as to if we are not just painting on metal when we use the group for its

colorability, maybe, but as long as the "painting" is good what difference does it make? Why is canvas any more suitable for painting than metal? Silver, copper, and gold also have a color that any conscientious metalsmith would consider in any piece that they make. Like more familiar metals they also have physical properties and characteristics that may be useful or limiting to the artist: titanium's lightness and strength could find uses in its own right; tantalum's and titanium's extreme hypoallergenicity may make them useful in producing jewelry for people with allergies to most other metals; niobium, tantalum, and especially hafnium have intrinsic monetary value, which is an associative "value" of jewelry; tantalum's unusual natural color may also be useful. The metals do have many limitations. Notably the titanium metal's resistance to forming on the jewelry scale, and their inability to be hard soldered. But their many unique characteristics must allow them a place in the store of materials from which the artist can draw on in their efforts to better express themselves.

